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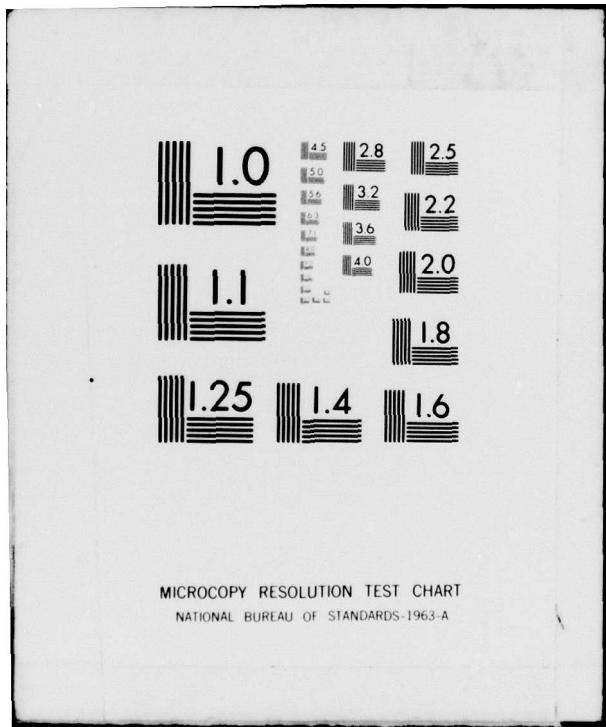
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The Importance of Transition States in  
Adsorption/Desorption Kinetics

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The equivalence of the "transition state," from the point of view of desorption from surfaces and "precursor state," from the point of view of adsorption is discussed. Applying detailed balancing to the problem helps to clarify the effect of intermediate states on the adsorption/desorption kinetics. The difficulty in considering this simple chemical kinetic problem in terms of a "rate limiting step" is illustrated.		

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THE IMPORTANCE OF TRANSITION STATES  
IN ADSORPTION/DESORPTION KINETICS

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1. INTRODUCTION

The concept of a "transition state" in chemical reaction paths is common to most theories of chemical rates. The concept permits the calculation of absolute reaction rates, at least for relatively simple cases such as unimolecular decomposition. The importance of transition states for chemical reactions on surfaces has also been frequently discussed. However, only recently have kinetic measurements of surface reaction rates been sufficiently refined to allow the transition state to be uniquely identified. The importance of transition states in adsorption/desorption kinetics has been revealed directly by measurements of pre-exponential factors for desorption and, indirectly, by measurements of sticking coefficients. Molecular beams have proven particularly useful for probing these and other details of the adsorption/desorption process.

The utility of treating adsorption and desorption together as a single microscopically reversible process has been amply demonstrated in molecular beam studies of scattering from single crystal surfaces.<sup>1,2</sup> By similar reasoning, Shannabarger,<sup>3</sup> King,<sup>4</sup> and Steinbruchel<sup>5</sup> have each noted that when "precursor" states affect adsorption kinetics, they must also play a similar role in desorption as well. More recently, Gorte and Schmidt<sup>6</sup> have developed several possible models for the adsorption/desorption path which proceeds through precursor states and have made comparisons with flash desorption data for systems where precursor intermediates are thought to play a role. A common feature in their analysis is a  $(1-\theta)^{-1}$  pre-exponential factor in the desorption rate which is a necessary consequence of the adsorption probability (sticking coefficient) being independent of coverage. They obtain this result by applying detailed balancing which is the consequence of microscopic reversibility for the special case of thermodynamic equilibrium.

In a closely related paper, published shortly after the work of Gorte and Schmidt, Menzel et al. report very careful and thorough experimental data for the kinetics of CO desorption from Ru(001).<sup>7</sup> Of particular interest is the observed coverage dependence of the pre-exponential factor which shows a sharp increase from  $\sim 10^{16}$  at low coverages to values approaching  $10^{20}$  near  $\theta = 0.5$ , followed by an abrupt drop to values in the range  $10^{14}$ - $10^{15}$  for  $0.5 < \theta < 1$ . They explain this behavior in terms of a transition state in the desorption path which has translational and rotational degrees of freedom whereas the chemisorbed state is "immobile." They get good quantitative agreement by assuming that the immobile layer becomes filled at  $\theta = 0.5$ . Their expression for the partition function of the immobile layer, taken from de Boer, also contains a term analogous to the  $(1-\theta)^{-1}$  factor predicted by Gorte and Schmidt for desorption via a precursor state, although their result is obtained from entirely different considerations.

The results discussed above further demonstrated the utility of applying the principle of microscopic reversibility to the adsorption/desorption process. Using this reasoning, the divergence in the pre-exponential for the desorption of CO from Ru(001) could have been predicted from measurements of the sticking coefficient versus coverage which we can conclude must be nearly constant up to  $\theta = 0.5$ . In the context of a discussion of "non-equilibrium" states it seems important to further develop this concept of microscopic reversibility, which applies equally to both equilibrium and non-equilibrium processes. The concept is particularly useful when our understanding of a process in one direction (e.g., adsorption) is more complete than our understanding of the reverse process (e.g., desorption). In particular, we will show that results such as those of Menzel, et al. which, at first, appear quite surprising are, in fact, the inevitable consequence of rather typical adsorption behavior which has been observed in molecular beam and other adsorption experiments.

## 2. MOLECULAR BEAM STUDIES OF ADSORPTION/DESORPTION

The author's understanding of gas-surface interface phenomena is based on a long involvement in molecular beam studies on surfaces. Perhaps one of the more notable results of these beam experiments was the first observation of distinctly non-cosine emission of hydrogen from smooth single crystal surfaces.<sup>1</sup> These results were, at first, quite surprising since the prevailing viewpoint was that the emission of fully accommodated species from surfaces should be random, i.e.,

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cosine. However, this viewpoint is not well-founded as has been subsequently discussed in some detail.<sup>8,9</sup> Indeed, further beam experiments have revealed that a number of gas-surface systems show non-random emission. Sharper-than-cosine emission has now been observed for hydrogen from Pt(111),<sup>1,10</sup> Ni(111),<sup>11</sup> Cu(111),<sup>12</sup> CO<sub>2</sub> from Pt(111)<sup>2</sup> and broader-than-cosine emission for CO and CO<sub>2</sub> from carbon covered Pt(111).<sup>13</sup> A model to explain these results was first presented by van Willigen.<sup>11</sup> This model involves a simple one-dimensional activation barrier in the adsorption path which predicts both an angular flux and energy dependence of adsorbed and desorbed particles. For the most part, the model has worked quite well in predicting the flux and energy dependences, both of which have been measured in a number of experiments.<sup>(1,11,12)</sup> In particular, the velocity distribution of CO<sub>2</sub> desorbing from polycrystalline platinum was measured and found to be equivalent to a temperature of 3500°K when the surface temperature was at 880°K.<sup>14</sup> This result had been previously predicted from measurements of the angular distribution of CO<sub>2</sub> from Pt(111).<sup>15,2</sup> While further studies of adsorption and desorption have raised questions regarding the role of surface impurities and crystal structure, the more general implications of these results remain intact.

One important departure of the data from the van Willigen model has been the dependence of velocity distribution on angle of emission.<sup>14</sup> Whereas the barrier model predicts an increase in average velocity away from the surface normal, the observed distributions (e.g., CO<sub>2</sub> from Pt) have shown a decrease in velocities toward glancing angles for those cases studied. This has been a cause for some concern since no alternative explanation has been advanced which accounts for both the angular and energy behavior. To account for this seeming discrepancy it is suggested that the desorption in those cases that have been studied is actually composed of two components. For example, CO<sub>2</sub> desorption from Pt(111) planes is accurately represented by  $\cos^6\theta$  whereas desorption from impurity and/or defect sites may be  $\cos \theta$ .<sup>2</sup> If 10% of the experimental surface gives rise to  $\cos \theta$  desorption then desorption near the normal will be predominantly via activated desorption while desorption at angles greater than 45° will be dominated by non-activated desorption. This explanation can be checked by careful measurements of the angle distribution of the desorption flux to determine if there is indeed a small cosine component. This, incidentally, raises another important point, and that is the need to characterize surfaces by scattering data, e.g.,

helium scattering distribution, in order to evaluate the relative perfection of nominally "single crystal" surfaces. Perfect single crystal planes are difficult if not impossible to obtain and imperfections of the order of 10% of the surface are not readily apparent unless the scattering is carefully reported. For example, if the perfect planar surface is 20% reflective, a typical value, and 10% of a particular surface area contains defects which give rise to diffuse scattering, then the total specular intensity is decreased by only 10% to a value of 18%. The diffuse nature of the inelastic scattering also makes this component difficult to recognize from the angular flux dependence. On the other hand, this same 10% of the surface may dominate in other processes on the surface so one should not glibly accept observations on even the most specular surfaces as necessarily being representative of single crystal planes.

### 3. TRANSITION STATES IN ADSORPTION/DESORPTION

While a comprehensive discussion of transition state theory is not appropriate or necessary here, some of the guiding principles should, perhaps, be mentioned. We will then attempt to develop a more physical interpretation that may be more palatable to those of us involved in studying the details of gas-surface interactions.

Transition state theory holds that, for a given chemical system, there exists a surface in phase space that separates reactants and products. On the reactant side of this surface, all configurations are equally probable. In other words, we assume quasi-equilibrium within reactant phase space. There is however, no such constraint on the products. Finally, transition state theory assumes that once the dividing surface has been crossed the products do not re-enter reactant space. The set of states that comprise the dividing surface is known as the "transition state."

Having presented this very generalized concept now consider, from three distinct viewpoints, the case of a molecule bound to a surface. Physically we picture the molecule as vibrating in some mode dictated by the potential well and energy of the system. At temperatures well above the Debye temperature, the probability of such a molecule having an energy greater than the bond strength  $Q$  is usually expressed  $e^{-\frac{Q}{RT}}$ . Note the  $e^{-\frac{Q}{RT}}$  is the fraction of particles with energy greater than  $Q$  in the exponential tail of the Boltzmann distribution. It is tempting to simply multiply this fraction by an appropriate "attempt frequency,"

say a vibrational frequency of  $10^{11}$ - $10^{14}$  sec $^{-1}$ , to obtain the expected frequency of bond breaking as a function of temperature. However, it is well known that this reasoning is incomplete and that the apparent rate of bond breaking can be orders of magnitude more rapid when there are additional degrees of freedom or states available at higher energies as is often the case. The Boltzmann distribution which the  $e^{-\frac{Q}{RT}}$  term is derived, is based on the principle that all points in phase space are equally probable and that the density of states is uniformly distributed. This is the case for an ideal gas but does not hold for most real systems. The consequence of the non-uniform distribution of states of real systems is that the energy distribution no longer has a simple exponential tail but is modified by the density of states distribution. In principle, this distribution can be obtained experimentally by measurements of heat capacity versus temperature but in many cases this is impractical. The problem is usually handled by adding a pre-exponential weighting factor to the  $e^{-\frac{Q}{RT}}$  term to account for the added area under the distribution which works approximately over a relatively narrow range of temperatures. To appreciate the magnitude of this pre-exponential factor it can be shown that, for the case of a typical adsorbate on a surface, this weighting factor can easily be as high as  $10^8$ .

The above problem can also be considered in terms of transition state theory as was done by Menzel et al. for the case of CO desorption from Ru(001). At equilibrium, the relative populations in the tightly bound immobile layer and transition state is weighted by their respective degrees of freedom or entropy. The partition function used by Menzel et al., taken from de Boer varies as  $(N_s - N)^{-1}$  where  $N_s$  is the number of available surface sites and  $N$  is the number of filled sites. This is, of course, equivalent to the  $(1-\theta)^{-1}$  dependence predicted by Gorte and Schmidt for desorption via a precursor state which they obtained by detailing balancing. At least in this case we can equate the physical precursor state with the conceptual transition state.

To give an idea of the actual relative populations of the precursor and bound states one can use typical values for the partition function

$f_p/f_b e^{-\frac{\Delta H}{RT}}$  of  $10^5$  for  $f_p/f_b$  and 40 kJ/mole for  $\Delta H$  which gives about equal populations for the precursor and bound states at 450°K. More correctly, this is the limit at low coverages since the  $(1-\theta)^{-1}$  term causes the

fraction to increase without limit near  $\theta = 1$ . It is, of course, the increased population of the transition or precursor state which accounts for the larger pre-exponential observed in flash desorption and other rates involving a change of phase.

More physical insight into the desorption process can be had if one considers the time reversed process of adsorption. From this viewpoint we readily picture the incoming CO molecules spending very little time in the precursor state at low surface coverages where the likelihood of striking an unoccupied site is high, but as the coverage increases, they spend more and more time diffusing across the surface looking for a "home." What holds them onto the surface is just a very shallow potential well and a large dose of entropic "glue." The fact of the adsorbing molecules spending more and more time in the precursor state is, as has been already pointed out, equivalent to a divergence in the pre-exponential for desorption.<sup>6</sup>

A question may arise as to the population of the precursor or transition state during a non-equilibrium process like flash desorption. This can be answered by mentally constructing the missing equilibrium adsorption flux. Since each flux contributes one-half the population of the precursor state, then in the absence of adsorption we have  $\sim 1/2$  the population in the precursor (transition) state that would exist at equilibrium. This result is not readily apparent when considered from the viewpoint of a "rate-limiting-step." If transitions to the precursor state are rate limiting then the population there is essentially zero, where, if transitions from the precursor to the gas phase are rate limiting, then the population of the precursor is near equilibrium but there is a small activation energy for desorption. This is but one example of the kind of bind that results from using the rate-limiting-step concept.

One final comment regarding transition state theory is in regard to its relationship to the "compensation effect" which is a ubiquitous phenomenon in activated processes. Compensation behavior is the tendency of the pre-exponential and activation energy of a process to vary together in a compensatory way, usually so that the overall rate remains relatively unchanged. The data of Menzel et al. for CO desorption versus coverage shows distinct compensation behavior and other examples of this effect in chemical kinetics and other areas abound. Possible reasons for a relationship between the pre-exponential factor and the activation

energy have been offered, and allusions to a more fundamental relationship have even been advanced.<sup>17</sup> Although these discussions generally involve rather arcane reasoning based in third and higher laws of thermodynamics, the regularity with which compensation behavior is seen does suggest that it is more than simply an empirical correlation. Interestingly in this regard, when calculations of reaction rates are made using transition state theory, compensation type behavior is the inevitable result of varying the arbitrarily chosen dividing surface between reactant and product.

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